

CLAIMS

1. A process for the fabrication of a microporous hydrophilic hollow fiber membrane from an ethylene-vinyl alcohol copolymer comprising the steps:

- (a) providing a spinning solution comprising 25 to 40 wt% ethylene-vinyl alcohol copolymer, 5 to 15 wt% low molecular weight pore-former, 5 to 15 wt% high molecular weight pore-former, 0.05 to 1 wt% water, and a solvent;
- (b) forming a spun hollow fiber by extruding said spinning solution through an orifice at a temperature above the precipitation point of the solution while simultaneously injecting a coagulating fluid through a needle located in said orifice;
- (c) drawing said spun hollow fiber into a quench bath of 15 to 35 wt% of an alcohol in water at a temperature of 40° to 65° C to form a hydrophilic microporous hollow fiber membrane;
- (d) rinsing said hydrophilic microporous hollow fiber membrane with water; and
- (e) drying said hydrophilic microporous hollow fiber membrane.

2. The process of claim 1 wherein said hollow fiber membrane is stretched during step (d).

3. The process of claim 2 wherein the degree of stretching during step (d) is from about 1.3 to about 3.0.

4. The process of claim 1 including an additional
5 step (f) comprising crosslinking said hollow fiber membrane.

5. The process of claim 4 wherein said crosslinking is conducted by a process comprising the steps:
10 (i) soaking said hollow fiber membrane in an aqueous solution of glutaraldehyde;
(ii) drying said hollow fiber membrane; and
(iii) annealing said hollow fiber membrane.

15 6. The process of claim 1 wherein the ethylene content of said ethylene-vinyl alcohol copolymer of step (a) is from 27 to 48 mol%.

20 7. The process of claim 1 wherein said low molecular weight pore-former of step (a) is selected from monohydric and polyhydric alcohols.

8. The process of claim 1 wherein said high molecular weight pore-former of step (a) is selected from
25 the group consisting of polyethylene glycol, polyethylene oxide, polypropylene glycol, polyvinylpyrrolidone and polyvinyl alcohol.

9. The process of claim 1 wherein said solvent of step (a) is selected from the group consisting of dimethylsulfoxide, dimethylformamide, dimethylacetamide, and N-methylpyrrolidone.

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10. The process of claim 1 wherein the weight ratio of said low molecular weight pore-former to said high molecular weight pore-former of step (a) is from about 0.3 to about 3.

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11. The process of claim 1 wherein said spinning solution of step (a) comprises 30 wt% ethylene-vinyl alcohol copolymer, 8.5 wt% ethylene glycol, 8.5 wt% polyethylene glycol, 0.1 wt% water and the solvent is dimethylsulfoxide.

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12. The process of claim 1 wherein said coagulating fluid of step (b) is selected from the group consisting of water, mixtures of water and alcohols, mixtures of water and solvent, and mixtures of water, alcohols and solvent.

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13. The process of claim 1 wherein said alcohol in step (c) is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, butanol, ethylene glycol and propylene glycol.

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14. The process of claim 13 wherein said quench bath of step (c) comprises 20 to 30 wt% isopropanol in water.

Sub A¹ → 15. The hollow fiber membrane product of the process of claim 1, 2 or 4.

5 16. The product of claim 15 wherein said hollow fiber membrane has a clean water flux greater than $2 \text{ m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ MPa}$ at 25°C , a wet tensile strength greater than about 180 g/fil, and a wet elongation at break greater than 40%.

Sub A² → 10 17. The process of any one of claims 1-14 further comprising, after the rinsing step (d) and before the drying step (e), the step:

15 (g) subjecting the rinsed hydrophilic microporous hollow fiber membrane to hot water treatment in a hot water bath at a temperature of 50°C to 100°C while relaxing tension on the fiber.

18. A process for improving membrane performance of a microporous hydrophilic hollow fiber membrane comprising the step:

20 (h) subjecting the hydrophilic microporous hollow fiber membrane obtained by the process of any one of claims 1-3 and 6-14 to hot water treatment in a hot water bath at a temperature of 50°C to 100°C while relaxing tension on the fiber

25 19. A process for the fabrication of a microporous hydrophilic hollow fiber membrane comprising crosslinking a hollow fiber membrane obtained by the process of claim

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20. The process of claim 19 wherein said crosslinking is conducted by a process comprising the
5 steps:

- (i) soaking said hollow fiber membrane in an aqueous solution of glutaraldehyde;
- (ii) drying said hollow fiber membrane; and
- (iii) annealing said hollow fiber membrane.

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Sub A3
21. The process of any one of claims 17-20 wherein, in the heat treating step (g) or (h), tension on the fiber is decreased to as close to zero as possible by using two
15 pulleys and allowing the fiber to sag between these pulleys.

22. The process of any one of claims 17-21 wherein, in the heat treating step (g) or (h), the hot water treatment temperature is not less than 80°C.

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23. (cancelled)

Sub A4
24. The hollow fiber membrane product of the process of any one of claims 17-23.